



Catalytic ozonation for the removal of organic contaminants in water on alumina



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ARTICLE INFO

Article history:

Received 19 June 2014

Received in revised form 1 October 2014

Accepted 3 October 2014

Available online 14 October 2014

Keywords:

Catalytic ozonation

Ibuprofen

VOCs

Alumina

Water

ABSTRACT

This study aims to understand the efficiency and role of adsorption of common water pollutants (volatile organic chemicals (VOCs), pharmaceuticals and carboxylic acids) in the catalytic ozonation process on γ -alumina. In order to understand the catalytic processes occurring, the effects of pH, hydroxyl radical scavengers, humic acids and phosphates on the efficiency of catalytic ozonation on alumina were studied. The results revealed that catalytic ozonation on alumina could substantially enhance the removal of ibuprofen and acetic acid when compared with ozonation alone. However, alumina did not catalyse the removal of VOCs. The adsorption of pollutants plays a key role in the effectiveness of this process. The presence of hydroxyl radical scavengers, phosphates and humic acids had a significant effect on the removal of pollutants on alumina. It is therefore suggested that catalytic ozonation of organic pollutants on alumina proceeds via a radical mechanism that involves reactions of hydroxyl radicals with pollutants adsorbed on the surface of alumina.

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1. Introduction

Heterogeneous catalytic ozonation is one of the oxidation techniques used to improve the efficiency of ozonation process. It has been successfully applied in the degradation of organic compounds such as aromatic hydrocarbons, pharmaceuticals, pesticides, dyes, and organic acids etc. Many materials such as activated carbons [1], Al_2O_3 [2] and TiO_2 [3] were utilised as heterogeneous catalysts. Despite years of research, the mechanisms of catalytic ozonation are largely unknown and there are many controversies in this area [4,5]. Therefore, it is indeed important to understand the process of catalytic ozonation in order to apply this technique on an industrial scale.

Ozonation on alumina oxides has been studied for several years with different types of pollutants. However, there are several, often contradictory, views on the catalytic activity of alumina. Some reports indicate that alumina does not catalyse the decomposition of aqueous ozone [6]. It is important to mention here that lack of ozone decomposition does not indicate the lack of catalytic activity [2]. In contrast, other reports indicated that alumina decomposes aqueous ozone leading to the production of hydroxyl radicals.

The surface hydroxyl groups on alumina were identified as active catalytic sites of ozone decomposition [7–9]. Qi et al. [10] also confirmed that alumina promotes the generation of hydroxyl radicals but the group claimed that surface hydroxyl groups of γ -alumina do not interact with aqueous ozone. It has been recently highlighted by Nawrocki et al. [11] that alkaline impurities present in alumina oxides can play an important role in ozone decomposition and hydroxyl radicals formation. This is because their desorption into the bulk solution results in pH changes of the aqueous solution, which then affect stability of molecular ozone in water. Therefore it is indeed important to monitor pH during the catalytic ozonation process.

The role of adsorption of pollutants on alumina is also not well understood [5]. Some reports suggested that adsorption plays an important role in the catalytic process [7,12,13]. Others indicated that adsorption could have a detrimental effect on the catalytic activity of alumina [14]. Therefore it is important to study catalytic ozonation on alumina in the presence of different types of pollutants with different affinity towards alumina's active surface sites.

This paper aims to understand mechanisms of ozonation on alumina in the presence of different types of pollutants. Among them are: volatile organic chemicals (VOCs), pharmaceuticals and carboxylic acids. VOCs are regulated pollutants that have been detected in drinking water [15]. Chlorinated aromatic compounds

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are highly toxic, widely used and are known to be highly resistant to ozonation [16]. Pharmaceuticals are emerging and still unregulated pollutants. Although they are present in trace quantities in the aquatic environment, long term exposure to these pollutants poses a potential risk to humans and aquatic life. Pharmaceuticals have also been detected in drinking water. Carboxylic acids are refractory to direct ozone attack and are known to be stable ozonation by-products of other organic pollutants [17]. The selection of acetic acid as target pollutant may further help to understand whether catalytic processes on alumina involve a radical mechanism or direct molecular ozone reactions. This is because acetic acid is highly resistant to direct ozone attack. In order to verify the catalytic processes occurring on alumina, the effect of initial pH, pH changes during the process and the effect of hydroxyl radical scavengers, humic acids and phosphates have also been investigated.

2. Experimental

2.1. Materials and reagents

γ -Alumina used in this work was supplied by Alcoa Inc, USA. Ibuprofen, humic acid, VOCs and acetic acid were obtained from Sigma-Aldrich. All chemicals were of analytical grade and were used without further purification.

2.2. Ozonation experiments

The ozonation experiments were conducted in a semi-continuous mode at room temperature (20 °C) as shown in Fig. S1 (column length, 70 cm; width, 31 mm; catalyst bed height, 5 cm). Aqueous solution (490 mL) spiked with organic pollutants (ibuprofen, 15 mg/L; acetic acid, 15 mg/L; or cumene, 19.1 ± 0.5 mg/L; 1,2-dichlorobenzene, 3.5 ± 0.3 mg/L; 1,2,4-trichlorobenzene, 0.5 ± 0.1 mg/L) was poured to the column containing 5.0 g of

alumina, and was recirculated at a flow rate of 15 mL/min over the period of 30 min. Ozone was produced from pure oxygen by AZCO HTU-5000GE-120 ozone generator and was continuously bubbled through the column by using a ceramic sparger at a flow rate of 0.1 mL/min (in the case of VOCs ozonation) or 0.5 mL/min (in the case of acetic acid and ibuprofen ozonation). Samples were collected at 5 min intervals and residual ozone was removed by quenching with 0.025 M Na₂SO₃. All the samples were filtered (PTFE 0.45 μ m syringe filter) prior to the analysis.

Possible loss of VOCs due to volatilization was also determined. A saturated solution of VOCs was used in the ozonation experiments and was prepared by directly spiking VOCs to a flask containing 1 L of ultrapure water [18].

Ozonation experiments in the presence of humic acid, tertiary butyl alcohol (TBA), and phosphates were performed as described above by adding 7 mg/L of humic acid or phosphates, or 50 mg/L of TBA to the semi-continuous reactor following the above procedure. It is important to mention here that the humic acid removal experiments in ozonation and the catalytic ozonation processes have been performed without the addition of VOCs and ibuprofen.

For reuse performance experiments, 490 mL solution containing ibuprofen (15 mg/L) was added to a column containing 5 g of the catalyst. After every 30 min a fresh solution of pollutants was introduced in a semi-continuous reactor. The cycle was repeated 12 times.

2.3. Adsorption experiments

The adsorption experiments were performed in the semi-continuous reactor by adding 490 mL of saturated VOCs solution (cumene, 19.1 ± 0.5 mg/L; 1,2-dichlorobenzene, 3.5 ± 0.3 mg/L; 1,2,4-trichlorobenzene, 0.5 ± 0.1 mg/L) or acetic acid (15 mg/L) or ibuprofen (15 mg/L) solutions to the semi-continuous column containing 5 g of catalyst. The solutions were recirculated for 30 min

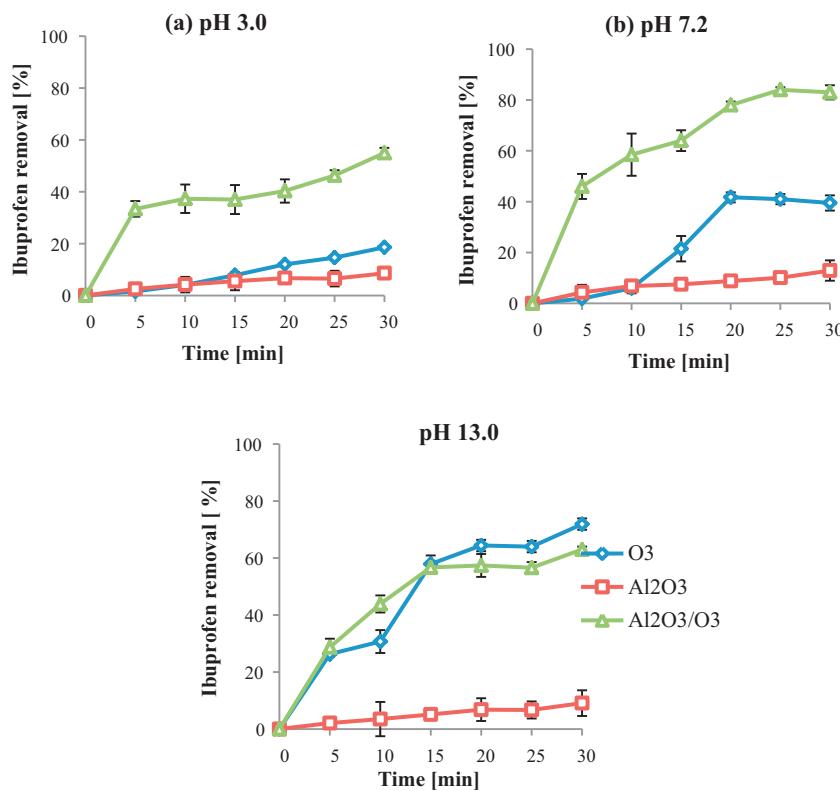


Fig. 1. Removal of ibuprofen by adsorption, ozonation alone and catalytic ozonation ($C_{0(ibu)} = 15$ mg/L; $O_3 = 0.5$ mg/min; $T = 20$ °C; pH = 3.0, 7.2 and 13.0; catalyst dose = 5.0 g; $V = 490$ mL).

(flow rate, 15 mL/min) and the samples were collected after every 5 min. All samples were filtered (PTFE 0.45 μm syringe filter) prior to the analysis.

3. Analytical procedures

3.1. Ozone dose

Ozone in the gas phase was determined by iodometric method [19]. For this purpose the gaseous ozone in in-gas and off-gas was continuously bubbled through a ceramic sparger into two sets of glass bottles, each filled with 200 mL of 2% KI (Fig. S1). After acidification of 200 mL of the 2% KI solution with 10 mL of 1 N HCl, the liberated iodine was titrated with standard 0.005 N $\text{Na}_2\text{S}_2\text{O}_3$ using a starch indicator.

3.2. Aqueous ozone

Aqueous ozone concentration was determined by the indigo method [19]. The difference in absorption of light at 600 nm between blank and sample was measured. The samples were

analysed with a Shimadzu UV-160A UV-Visible Spectrophotometer. The calibration curve was established before analysis.

3.3. Analysis of VOCs

Concentrations of VOCs were determined by gas chromatography coupled with mass spectrophotometry (GC/MS, Agilent) as described previously [18]. Limits of quantification for cumene, dichlorobenzene and trichlorobenzene were 0.8 ppm, 0.5 ppm and 0.4 ppm respectively. Limits of detection for cumene, dichlorobenzene and trichlorobenzene were 0.4 ppm, 0.3 ppm and 0.1 ppm respectively. The RSD was less than 5%.

3.4. Analysis of ibuprofen

Concentrations of ibuprofen were analysed by Gilson 506C HPLC equipped with UV-Visible detector and Phenomenex Kinetex 2.6 μm C_{18} 100 \AA column (100 mm \times 4.60 mm). The flow rate of mobile phase was of 0.4 mL/min and injection volume was 30 μL . The mobile phase was methanol/water (70: 30 v/v) modified with 1% acetic acid (pH 3). Limits of detection and quantification were 0.2 ppm and 0.5 ppm respectively. The RSD was less than 5%.

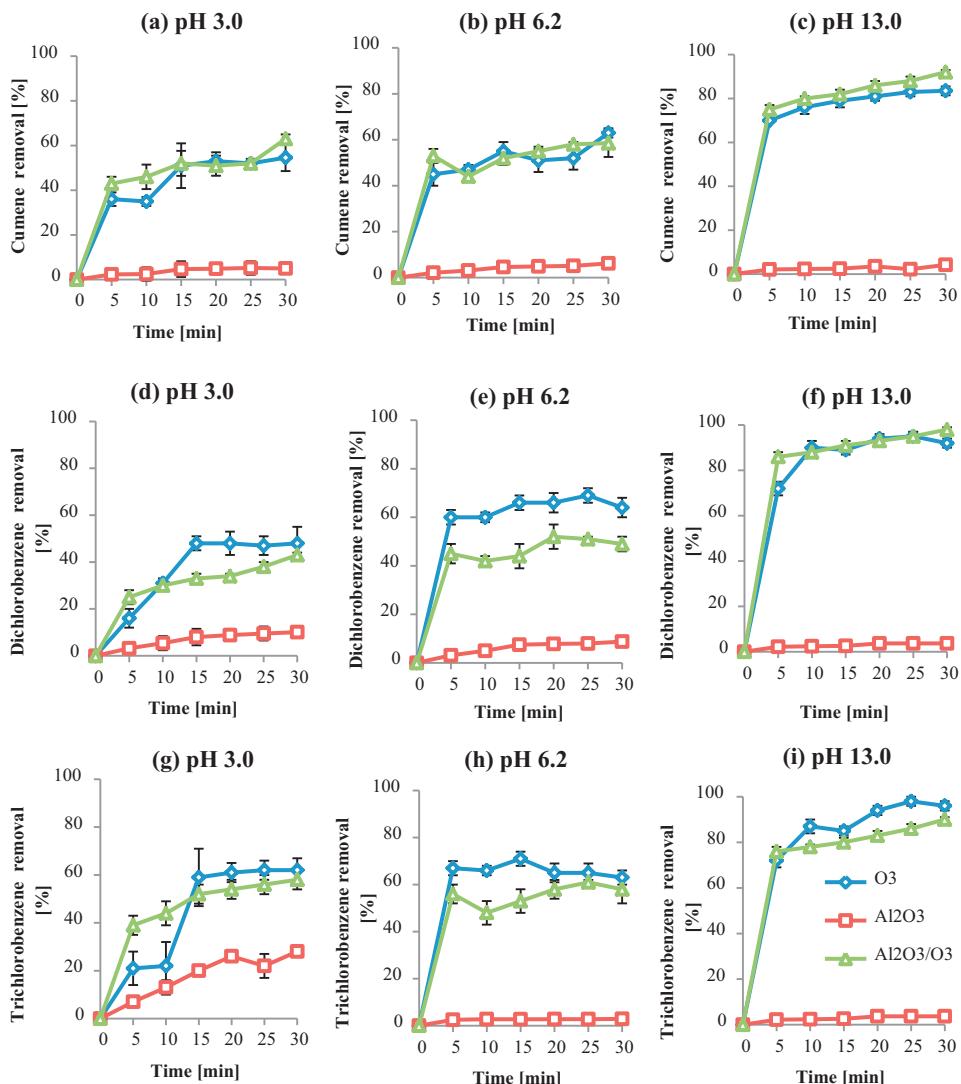


Fig. 2. Effect of pH on VOCs removal by adsorption, ozonation alone and ozonation in the presence of alumina ($C_{0(\text{cum})} = 19.2 \text{ mg/L}$, $C_{0(\text{DCB})} = 3.5 \text{ mg/L}$, and $C_{0(\text{TCB})} = 0.5 \text{ mg/L}$; $T = 20^\circ\text{C}$; pH = 3.0, 6.2 and 13.0; $\text{pH}_{30\text{ min}} = \text{pH}_0 \pm 0.3$; catalyst amount = 5 g; $V = 490 \text{ mL}$; $\text{O}_3 = 0.1 \text{ mg/min}$).

3.5. Analysis of organic acids

Acetic acid and other organic acids were analysed with the use of Dionex DX-120 ion chromatograph, equipped with Ion Pac-ICE-ASI 9 mm × 250 mm column and AMMS-TCE 300 anion micro membrane suppressor. Heptafluorobutyric acid (1.0 mM) was used as eluent and tetrabutylammonium hydroxide (5 mM) was used as regenerant. The injection volume was 25 μ L, cell temperature was 30 °C and eluent flow and regenerant rate were 0.82 mL/min and 5 mL/min respectively [18]. The limits of detection and quantification for acetic acid were 0.3 ppm and 0.5 ppm respectively. The RSD was less than 5%.

3.6. Analysis of phosphates

Phosphate concentrations were determined by ion chromatography using a DIONEX DX-120 system with Ion Pac As14 analytical column (4 mm × 250 mm) and Ion Pac AG14 guard column (4 mm × 250 mm) coupled to an ED-50A electrochemical detector (Dionex, USA) [18]. Limits of detection and quantification for phosphates were 0.3 ppm and 0.6 ppm respectively. The RSD was less than 5%.

3.7. Analysis of humic acid

Humic acid was analysed by the measurement of absorbance at 254 nm with the usage of Shimadzu UV-160A UV-Vis Spectrophotometer. The sample was filtered and was placed in a 1.0 cm quartz cell. The calibration curve was established before analysis. The limits of detection and quantification were 0.5 ppm and 0.9 ppm respectively. The RSD was less than 5%.

4. Results and discussion

4.1. Physicochemical properties of alumina

The surface area of alumina used was 190 m^2/g , the average pore size was found to be 47.8 Å and the point of zero charge was determined by mass transfer method and was found to be 8.9 [7]. The surface morphology of alumina before and after its reuse was characterised by scanning electron microscopy (SEM). The SEM studies were conducted using a JEOL JSM-6060 microscope. The images were taken with 100 μ A emission current by a tungsten filament and 12 kV of accelerator voltage. More information on alumina's properties can be found in our previous work [7] and Table S1.

4.2. Catalytic ozonation of pharmaceuticals, VOCs and carboxylic acids on alumina

4.2.1. Catalytic ozonation of ibuprofen

Catalytic ozonation and adsorption of ibuprofen on alumina was studied at different initial pH values. In this study the pH values were selected by considering the ionised and protonated forms of ibuprofen (pK_a) and charge on alumina (pH_{PZC}). The results presented in Fig. 1 reveal that ibuprofen shows higher adsorption on alumina at pH 7.2 than at pH 3.0 and 13.0. For example, at pH 3.0 only 8.6% ibuprofen was adsorbed in 30 min (Fig. 1a) and reached 13% at pH 7.2. This may be explained with respect to the ionization of ibuprofen and alumina at different pH values. At pH 7.2 ibuprofen is ionised (negatively charged as pK_a of ibuprofen is 4.9), which facilitates electrostatic interactions between ibuprofen and positively charged alumina at this pH value ($\text{pH}_{\text{PZC}} = 8.9$) [20]. At pH 13.0, ibuprofen is negatively charged, which results in weaker interactions with alumina which is negatively charged at pH 13.0. An alternate explanation could be that the low adsorption of ibuprofen

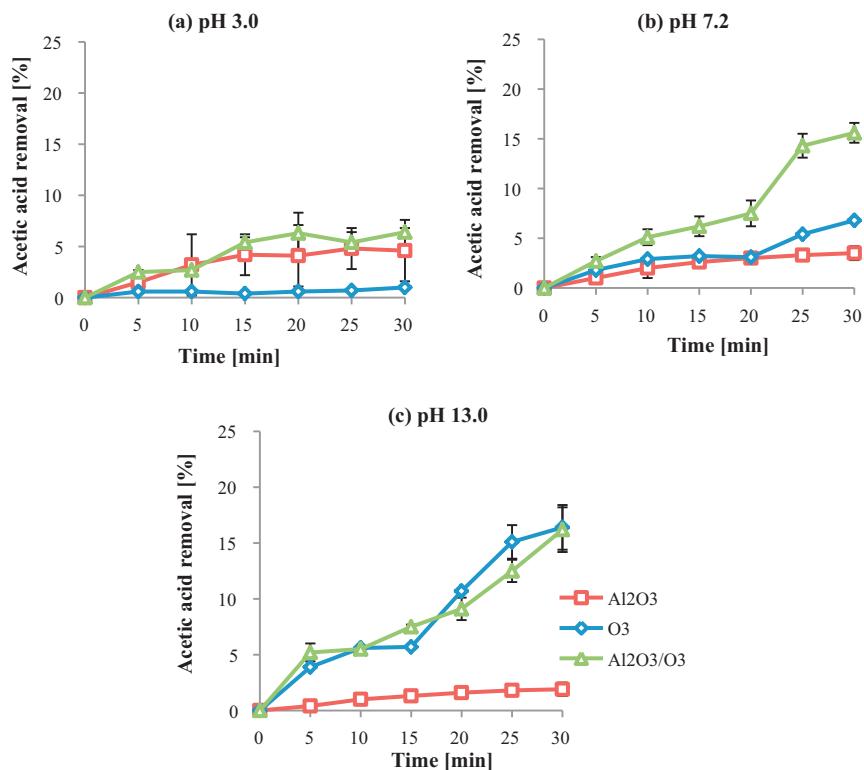


Fig. 3. Removal of acetic acid by adsorption, ozonation alone and catalytic ozonation ($C_{\text{O(ace)}} = 15 \text{ mg/L}$; $\text{O}_3 = 0.5 \text{ mg/min}$; $T = 20^\circ\text{C}$; $\text{pH} = 3.0, 7.2$ and 13.0 ; Catalyst dose = 5.0 g; $V = 490 \text{ mL}$).

at pH 13.0 may be due to the influence of adsorbed hydroxide ions on the surface of alumina.

The results presented in Fig. 1 further show that catalytic ozonation on alumina was effective (when compared to ozonation alone) at pH 3.0 and 7.2, with the highest activity at pH 7.2. For example, 83% of ibuprofen was removed in 30 min of ozonation in the presence of alumina (Fig. 1b) and at pH 3.0 the removal of ibuprofen was reduced to 58% (Fig. 1a). Previous reports indicate that alumina's activity increased near the point of zero charge of alumina [7–9]. The adsorption of ibuprofen on alumina is also an important factor, as ibuprofen has a high adsorption at pH 7.2 (Fig. 1b). It is important to mention here that ibuprofen removal studies on alumina show the opposite results when compared with zeolites [18]. It was reported that zeolites show high catalytic activity at pH 3.0. This further supports our hypothesis that adsorption of pollutants on catalytic surfaces plays a vital role, whether the catalyst operates through a radical mechanism or molecular ozone reactions on the catalyst surface. However, alumina did not show any activity at a basic pH of 13. This may be due to the high concentration of OH[−] [21]. Indeed, aqueous ozone concentrations were found to be very low at pH 13.0 during both catalytic ozonation and ozonation alone

(Fig. S2). As a result, any reaction of ibuprofen with ozone on the surface of the catalyst would be unlikely. Additionally, adsorption of ibuprofen was also low at pH 13.0 which may be also responsible for the lack of catalytic activity at this pH.

Furthermore, it is important to mention here that formation of organic acids was not observed during the catalytic ozonation process in the presence of alumina. Previous findings indicate the formation of organic acids during catalytic ozonation of ibuprofen on zeolites. Based on previous reports [14], this may be due to the adsorption and degradation of organic acids during catalytic ozonation on alumina.

4.2.2. Catalytic ozonation of VOCs

Catalytic ozonation of VOCs on alumina was studied at selected pH values. The results presented in Fig. 2 show that alumina does not show catalytic activity for VOCs. This may be due to the low adsorption of VOCs on alumina. From these results it can be hypothesized that adsorption of pollutants on the surface of catalyst is an important step. This is in contrast to studies by Ernst et al. [14]. Previous reports indicate that alumina is not a good catalyst for hydrophobic compounds [12,22]. This may be due to the lack of

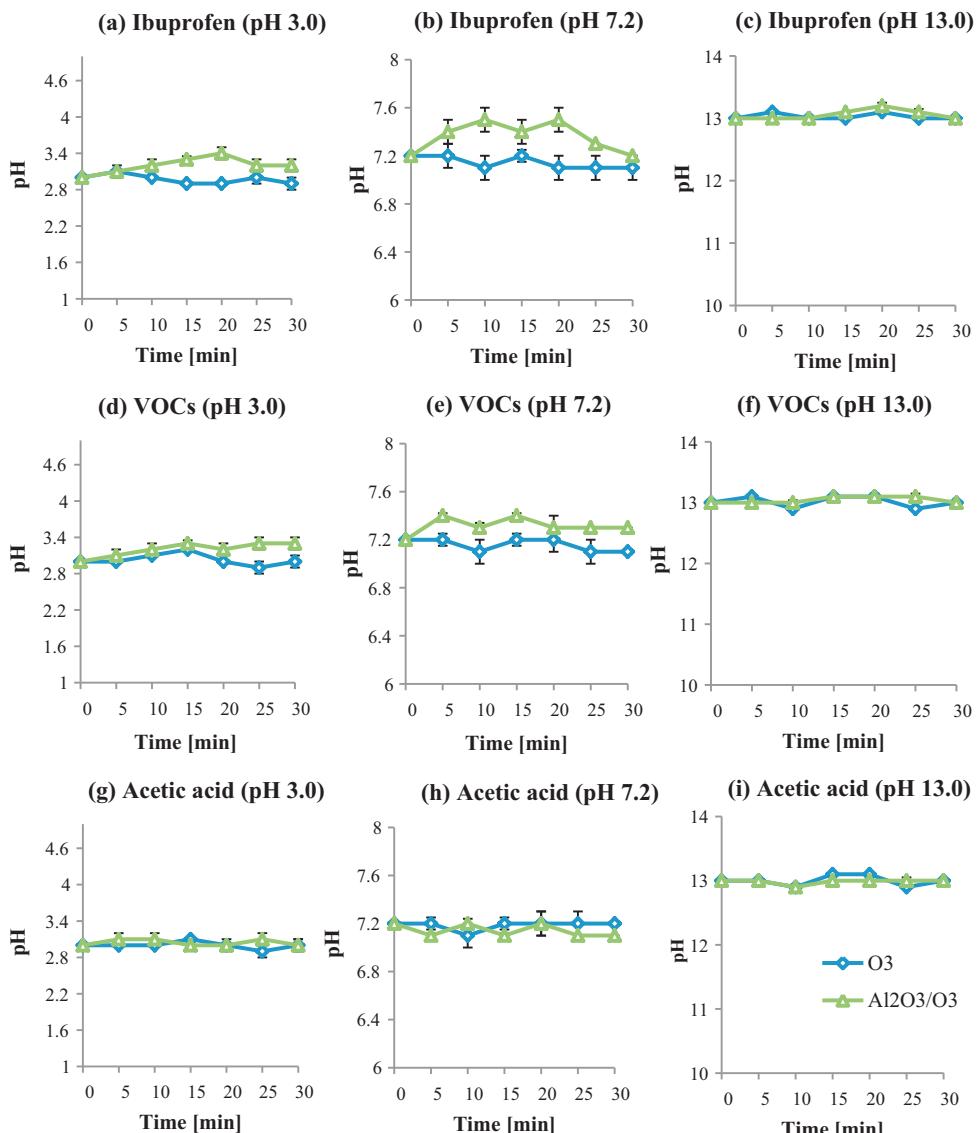


Fig. 4. pH changes during ozonation and catalytic ozonation of pollutants in the presence of alumina ($T=20^{\circ}\text{C}$; initial pH = 3.0, 7.2 and 13.0; $t=30$ min; $\text{O}_3=0.5$ mg/min, $\text{O}_3=0.1$ mg/min; catalyst 5 g; $V=490$ mL).

adsorption of hydrophobic compounds on the surface of alumina. The aqueous ozone decomposition studies (Fig. S3) indicate that although more ozone decomposition is observed during the catalytic process, still, a lack of catalytic activity has been observed in the case of VOCs. This suggests that surface reactions indeed play a vital role in the catalytic ozonation process. It was previously reported that high silica zeolites are both good adsorbents of studied organic contaminants and good catalysts of ozonation [18], which further supports our hypothesis that adsorption of pollutants plays a vital role. It is also important to note that no significant change in the pH of solution was observed in all experiments after 30 min reaction time.

It is important to mention here, based on undertaken adsorption studies, that adsorption of pollutants on the surface of the catalyst may play an important role in the catalytic processes. The above results clearly indicate that ibuprofen shows much higher adsorption on alumina when compared with VOCs. For example, maximum adsorption of ibuprofen was 0.4 mg/g (pH = 7.2), however, it only denoted 0.2 mg/g (pH = 6.2), 0.07 mg/g (pH = 3.0) and 0.03 mg/g (pH = 3.0) in the case of cumene, dichlorobenzene and trichlorobenzene respectively. However, low adsorption may not be the only reason for the lack of catalytic activity in the case of VOCs. Therefore, an alternative explanation could be that molecular ozone reactions may be favourable in the case of VOCs.

4.2.3. Catalytic ozonation of acetic acid

Reactions of ozone with organic compounds lead to the formation of by-products and among them the most common are ketones, aldehydes and carboxylic acids [18]. Carboxylic acids are the most stable ozonation by products. Therefore, ozonation alone is not sufficient for their effective degradation [1]. It was therefore decided to study their removal during catalytic ozonation on alumina. Acetic acid was chosen as a target compound.

The results presented in Fig. 3 show that the removal of acetic acid is higher after ozonation on alumina when compared to ozonation alone. The efficiency of the process is pH dependent. The highest removal has been observed, similarly to ibuprofen, at pH 7.2 (Fig. 3b). For example, 19% of acetic acid was removed in the case of ozonation in the presence of alumina at pH 7.2 and only 6.4% and 16.2% were removed at pH 3.0 and 13 respectively. It was previously reported that catalytic activity of alumina increases with the increase in pH and is the highest near the point of zero charge of alumina [7–9], which supports our findings. Furthermore, in the current investigation, the adsorption process was also found to be pH dependent and was the highest at pH 7.2. For example, the percentage adsorption of acetic acid on alumina was 5% and 1.9% at pH 3.0 and 13 respectively (in 30 min, Fig. 3a) and reached 7% at pH 7.2. This is to be expected as acetic acid is ionised at pH higher than its pK_a 4.7 and alumina is positively charged at pH $< p_{ZPC}$ 8.9.

The above results indicate that catalytic ozonation of acetic acid on alumina does not involve molecular ozone reactions. If this was the case, alumina would show some catalytic activity at acidic pH. This could be possible through a radical mechanism. It has been reported that organic acids can adsorb on the surface of alumina, replacing surface hydroxyl groups [23]. The observed lack of catalytic activity at pH 3.0 could possibly be due to the exchange of surface hydroxyl groups of alumina by ligand exchange process with acetic acid [23], which are considered to be the active sites [7–9]. The current results do not conclusively indicate which could be the active sites of alumina. However, the removal of ozone resistant acetic acid clearly indicates that alumina catalyses the decomposition of acetic acid.

An alternative explanation could be that the decomposition of acetic acid increases with the increase of pH due to the production of hydroxyl radicals inside the solution. These radicals concentrate on the surface of alumina [10] and degrade the adsorbed pollutants.

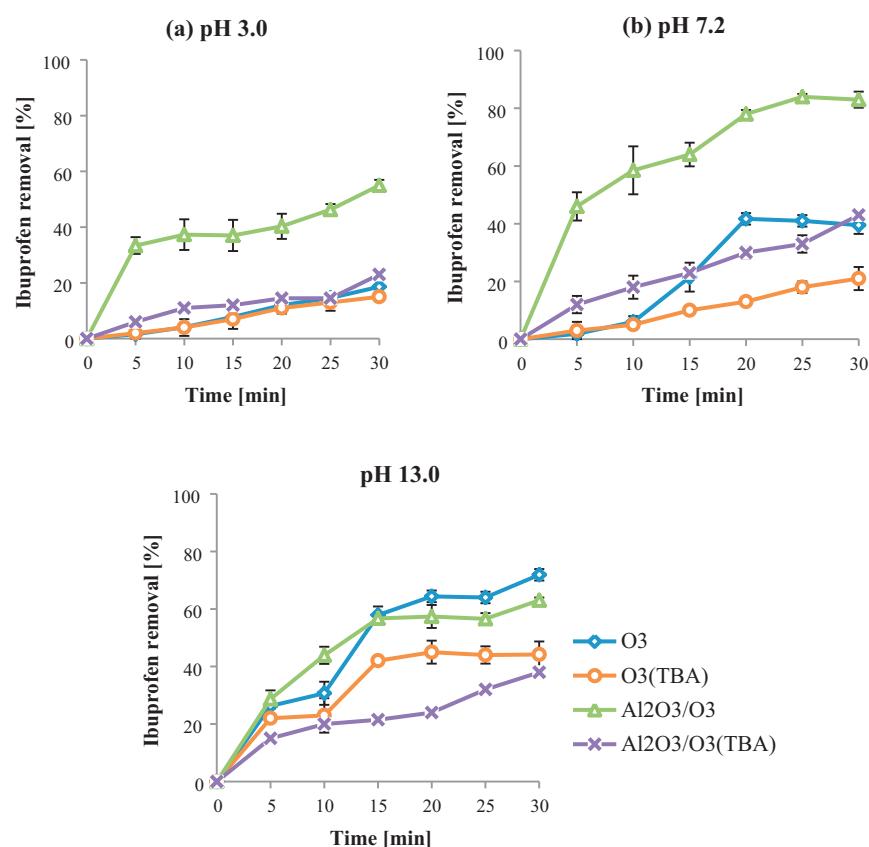


Fig. 5. Effect of TBA on ibuprofen removal by O_3 and Al_2O_3/O_3 ($C_{0(ibu)} = 15 \text{ mg/L}$; $T = 20^\circ\text{C}$; pH = 3.0, 7.2 and 13.0; $t = 30 \text{ min}$; $O_3 = 0.5 \text{ mg/min}$; TBA = 50 mg/L; $V = 490 \text{ mL}$).

The lack of catalytic activity of alumina at pH 13.0 (Fig. 3c) may be due to the lowest adsorption of acetic acid at this pH.

It is worth mentioning that previous reports indicate that removal of acetic acid does not show any significant improvements regardless of the pH by using catalytic ozonation on ZSM-5 zeolites [18]. This may be because acetic acid is refractory to molecular ozone, which further supports our hypothesis that decomposition of pollutants on alumina involves radical mechanisms.

4.3. pH changes during the ozonation and catalytic ozonation process

It has been recently reported by Nawrocki and Fiolek [11] that higher ozone decomposition in the presence of alumina as compared with ozonation alone may be due to alkaline contaminants present on the surface of alumina, which when desorbed from alumina's surface to the bulk solution can change pH of solution and these pH changes can lead to increased ozone decomposition rates [11]. Therefore, it is important to monitor pH during the ozonation and catalytic ozonation process. The results presented in Fig. 4 indicate that in the current research no significant change in pH was observed during ozonation alone and catalytic ozonation on alumina. It is, however, important to mention that Nawrocki et al. [11] studied pH changes and ozone decomposition in the absence of pollutants. In the current investigation pH changes have been studied in the presence of pollutants. It is worth noting that a small increase in initial pH followed by a decrease of pH was observed in the case of catalytic ozonation of ibuprofen and VOCs (Fig. 4b, e). Such a phenomenon could be attributed to desorption of contaminants leading to a slight increase of pH followed by formation of

acidic by-products, which then led to the decrease of pH [24] but further research is needed to verify this hypothesis. Fig. 4 further shows that in the case of catalytic ozonation of acetic acid, no significant change in pH was observed. This may be due the buffering effect of acetic acid. The acetic acid removal studies indicate that although no significant change in pH was observed the catalytic effect is still significant at pH 7.2 (Fig. 3b).

4.4. Mechanisms of catalytic ozonation

4.4.1. Effect of tert-butyl alcohol on the efficiency of catalytic ozonation on alumina

To determine whether alumina facilitates ozone decomposition and hydroxyl radicals formation tert-butyl alcohol (TBA) was used due to its strong radical scavenger ability [10].

The results presented in Fig. 5 indicate that in the case of ibuprofen ozonation on alumina, TBA inhibits the removal of ibuprofen and this effect is more prominent with the increase in pH. For example, at pH 7.2 the removal of ibuprofen was 82% in 30 min and in the presence of TBA it reduced to 43% (Fig. 5a). This is to be expected as at higher pH, due to the presence of hydroxide ions, free hydroxyl radicals are more readily formed. Such observations indicating the inhibition of catalytic activity of alumina were reported in several papers [7–10].

The results presented in Fig. 6 show that in the case of catalytic ozonation of cumene, TBA also decreases ozonation efficiency but this effect is much less prominent. This may be due to the lack of adsorption of cumene on alumina. The hydroxide radicals from the solution may concentrate on or near the alumina surface [10,25] which could lead to high removal of adsorbed pollutants.

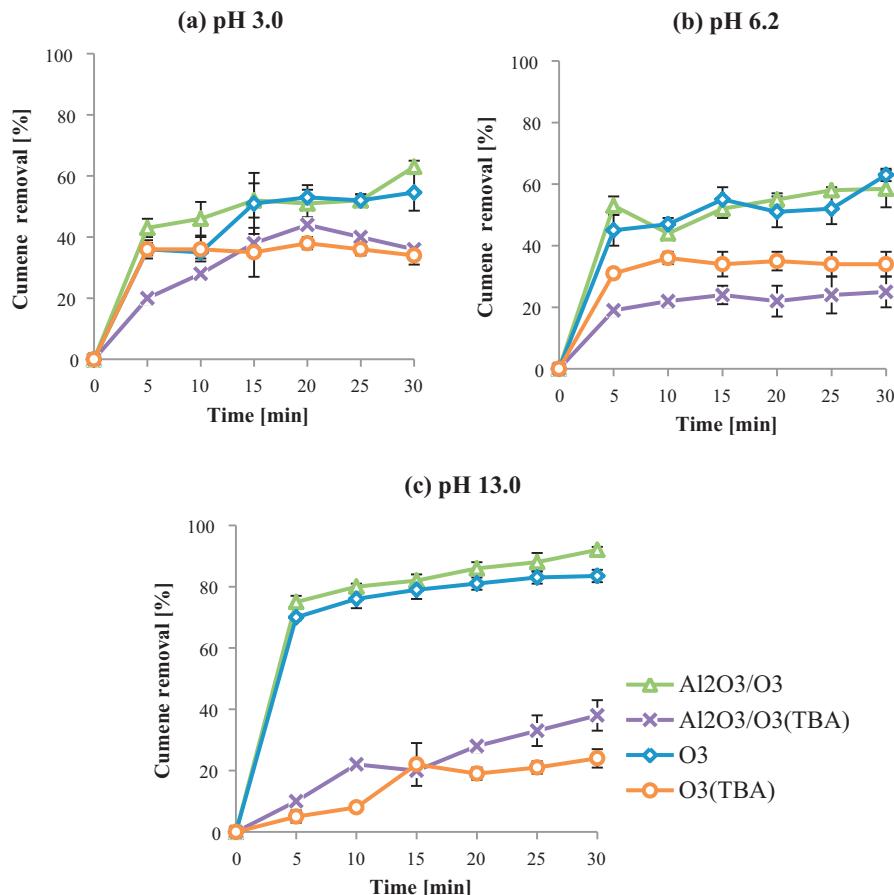


Fig. 6. Effect of TBA on cumene removal by O_3 and Al_2O_3/O_3 ($C_{0(cum)} = 19.2 \text{ mg/L}$; $T = 20^\circ\text{C}$; pH = 3.0, 6.2 and 13.0; $pH_{30\text{min}} = pH_0 \pm 0.3$; TBA = 50 mg/L; $V = 490 \text{ mL}$; $O_3 = 0.1 \text{ mg/min}$).

Our alternate explanation could be that molecular ozone reactions may be favourable in the case of studied hydrocarbons.

It is important to mention that ozone decomposition in the absence of pollutants was studied in our previous work [7]. It was concluded that alumina decomposes the aqueous ozone in the absence of pollutants leading to the generation of hydroxyl radicals. The results presented in this work further support this hypothesis.

4.4.2. Effect of phosphates on the efficiency of catalytic ozonation on alumina

Phosphates, sulfates, carbonates and bicarbonates are commonly present in drinking waters. They are not only responsible for scavenging hydroxyl radicals in the solution, but additionally, they may also adsorb on the catalyst surface and poison it [7]. It can be observed in Fig. 7 that phosphates significantly affect the efficiency of catalytic ozonation of ibuprofen on alumina and this effect is the most pronounced at pH 3.0 (Fig. 7a).

The adsorption results indicate that alumina has a high adsorption capacity (<23%) towards phosphates (Fig. S5), which decreases with the increase of pH. Such a phenomenon results from the presence of hydroxide ions that can suppress the adsorption of phosphates due to the fact that hydroxide ions are stronger bases [7,20,21] (Fig. 8).

4.4.3. Effect of humic acids on the efficiency of catalytic ozonation on alumina

Humic acids (HAs) are fundamental components of natural organic matter and they are widely present in natural waters. It is therefore of importance to study their possible effects on catalytic ozonation in the presence of alumina. It has been previously

reported that ozonation in the presence of alumina can catalyse the removal of natural organic matter in water [2]. In this work, the effect of humic acid was studied in the catalytic ozonation of ibuprofen and VOCs (cumene).

The results presented in Fig. 9a, indicate that removal of ibuprofen in the presence of alumina decreases when humic acids are present in the solution. For example, the removal of ibuprofen was 83% (after 30 min ozonation time) in the absence of HA and decreased to 60% in the presence of humic acid. It is worth emphasising that alumina also catalyses the removal of HA (Fig. 9c). The decrease in the removal of ibuprofen may be due to the adsorption of HA on alumina surface and/or competition with ibuprofen for active oxidative species. Similar results have been obtained during ozonation of cumene on alumina (Fig. 9b). The removal of ibuprofen and cumene in the presence of humic acid has been studied at pH 7.2 and 6.2 respectively (Fig. 9a, b). At this pH a large part of phenolic and carboxylic groups of humic acid are deprotonated and have negative charge on them, while the alumina at this pH will be positively charged, which will facilitate sorption of humic acid on the surface of alumina. It is important to mention that no significant change in pH ($\text{pH} \pm 0.3$) was observed during the above mentioned ozonation and catalytic ozonation processes.

4.4.4. Kinetics of catalytic ozonation

The kinetic studies of catalytic ozonation for the removal of ibuprofen, cumene and acetic acid were conducted (Table 1). Pines et al. [25] studied the decay rates of p-chlorobenzoic acid in ozonation alone and catalytic ozonation process using metal oxides. Ozone decay rates for both processes were found to fit a pseudo-first order decay. In current investigation the decay of pollutants

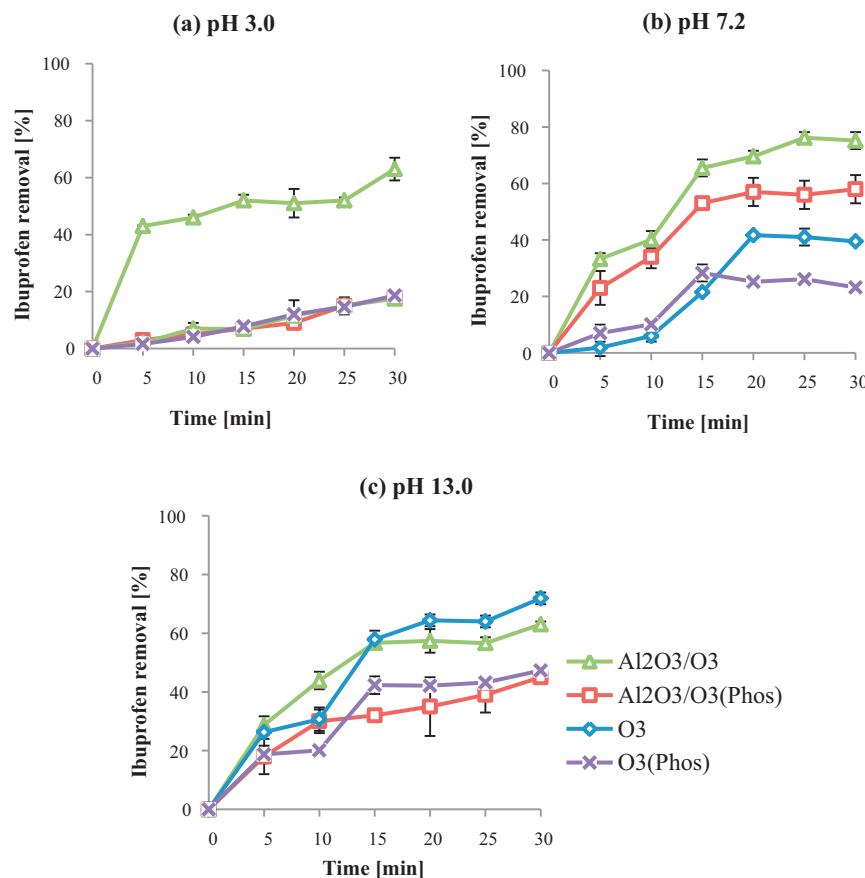


Fig. 7. Effect of phosphates on ibuprofen removal by O_3 and $\text{Al}_2\text{O}_3/\text{O}_3$ ($C_{\text{O}(\text{ibu})} = 15 \text{ mg/L}$; $T = 20^\circ\text{C}$; $\text{pH} = 3.0, 7.2$ and 13.0 ; $t = 30 \text{ min}$; $\text{O}_3 = 0.5 \text{ mg/L}$; phosphates = 50 mg/L ; $V = 490 \text{ mL}$).

Table 1First order decomposition rates of cumene, ibuprofen and acetic acid in O_3 and Al_2O_3/O_3 processes.

Process	$k(10^{-2} \text{ min}^{-1})$								
	pH = 3.0			pH = 6.2, 7.2			pH = 13.0		
	Ibuprofen	Acetic acid	Cumene	Ibuprofen	Acetic acid	Cumene	Ibuprofen	Acetic acid	Cumene
O_3	0.73 ± 0.04	0.20 ± 0.1	1.37 ± 0.1	2.15 ± 0.1	0.16 ± 0.05	9.33 ± 0.2	3.89 ± 0.1	0.57 ± 0.1	1.74 ± 0.1
Al_2O_3/O_3	1.43 ± 0.05	0.16 ± 0.1	1.42 ± 0.1	4.81 ± 0.1	0.61 ± 0.04	8.64 ± 0.4	2.42 ± 0.1	0.50 ± 0.1	1.85 ± 0.3

was also found to fit pseudo-first order kinetics. Therefore, by applying pseudo-first order considerations [25], first order rate constants for the removal of pollutants were determined. The results clearly indicate that ibuprofen and acetic acid decomposition rates are higher in the case of catalytic ozonation as compared with ozonation alone (at pH 3 and 7.2). However, the rate constant values for cumene decomposition in single ozonation and the catalytic processes were significantly different. This could possibly be due to the lack of adsorption of cumene on the surface of alumina. Previous kinetic studies [26] on catalytic ozonation in the presence of alumina indicate that surface reactions are important in catalytic process. Furthermore, our previous work [7] reporting ozone decay rates in the absence of pollutants proved that ozone decay rates in the presence of alumina are higher when compared to ozonation alone. Above findings support our hypothesis that catalytic ozonation on alumina proceeds via a hydroxyl radical mechanism and that surface reactions are important for the effective removal of pollutants on alumina.

4.4.5. Proposed mechanism

The results presented in this work indicate that catalytic ozonation on alumina proceeds via a radical mechanism as indicated by TBA effect. This is in agreement with previous findings [7–9,21] and additionally the removal of ozone refractory acetic acid further supports our hypothesis. Previous reports indicate that alumina may decompose aqueous ozone leading to the production of active oxygen species [7–9,21]. Surface hydroxyl groups were found to be the active site [7–9,21]. Qi et al. [10] also confirmed that alumina promotes the generation of hydroxyl radicals but the group claimed that surface hydroxyl groups of alumina do not interact with ozone. Some reports contradict this and suggest that aqueous ozone is not decomposed by alumina [6,11]. Other reports further suggest that molecular ozone reactions may be involved [2,11]. The results presented in this work clearly indicate that ozonation in the presence of alumina involves radical mechanisms. The results further indicate that adsorption of pollutants on the surface of catalyst is a vital step in the catalytic ozonation process.

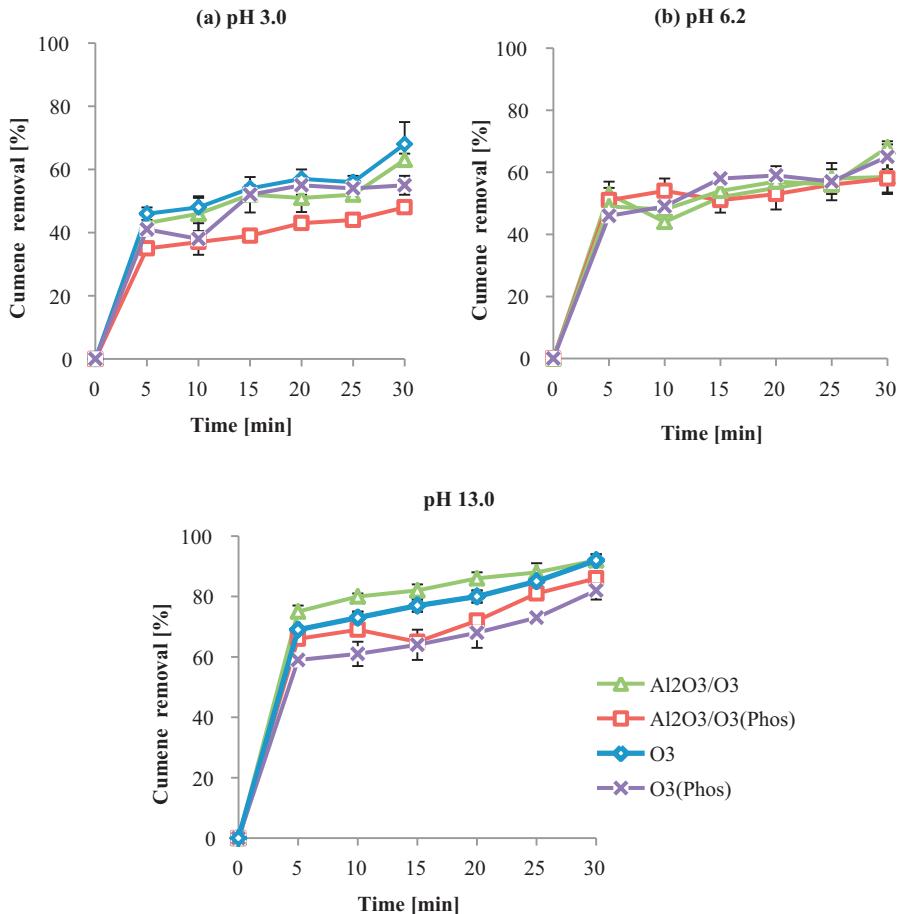


Fig. 8. Effect of phosphates on cumene removal by O_3 and Al_2O_3/O_3 ($C_{0(cum)} = 19.5 \text{ mg/L}$; $T = 20^\circ\text{C}$; pH = 3.0, 6.2 and 13.0; $t = 30 \text{ min}$; $O_3 = 0.1 \text{ mg/L}$; phosphates = 50 mg/L; $V = 490 \text{ mL}$).

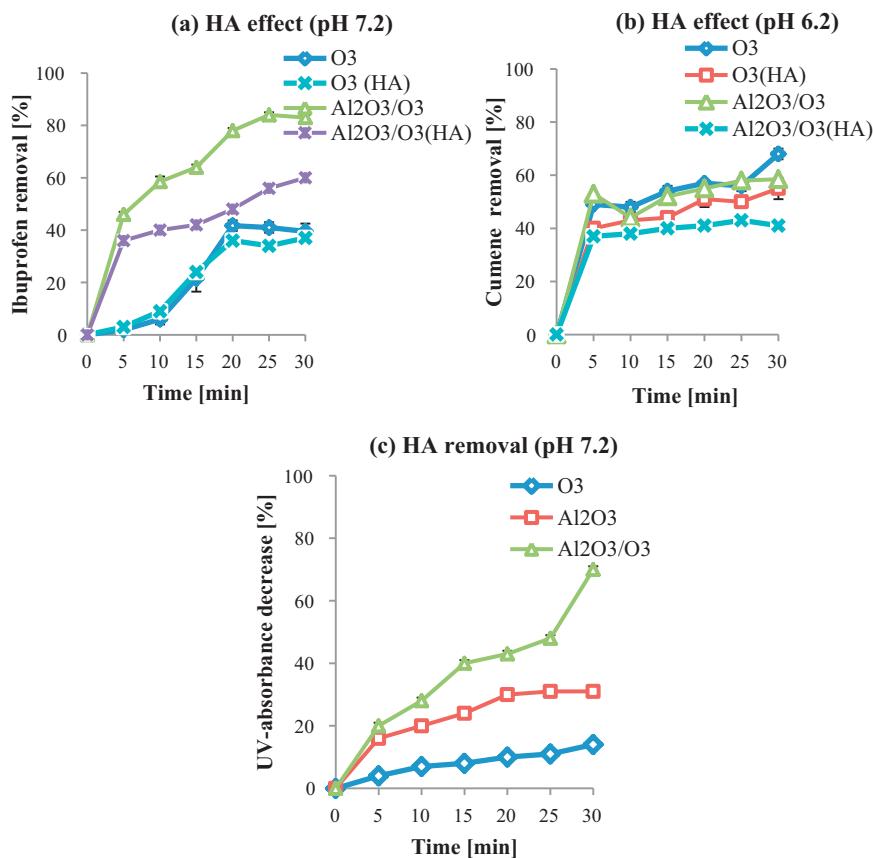


Fig. 9. Effect of humic acid on ibuprofen and cumene removal by O₃ and Al₂O₃/O₃ ($C_{0(\text{ibu})} = 15 \text{ mg/L}$; $C_{0(\text{cu})} = 19.2 \text{ mg/L}$; $C_{0(\text{HA})} = 7.0 \text{ mg/L}$; $T = 20^\circ\text{C}$; $O_3 = 0.5 \text{ mg/L}$; pH = 7.2, 6.2; catalyst = 5.0 g; $V = 490 \text{ mL}$).

Two mechanisms may be hypothesised based on the previous reports and results presented in this paper. The first hypothesis could be that alumina promotes the decomposition of aqueous ozone leading to the production of hydroxyl radicals and other oxidative species. Surface hydroxyl groups on alumina may [7–9] or may not be the active sites [10]. However, the removal of pollutants in the presence of phosphates clearly suggests that surface hydroxyl groups on alumina are likely to be the active sites [7,21]. Others have suggested that formed radicals may adsorb on the surface of alumina [10] and react with the adsorbed pollutants.

The other proposed mechanism assumes that alumina does not decompose aqueous ozone [6,11]. However, hydroxyl radicals formed in bulk solution may react with the pollutants in the solution as well as may adsorb on the surface of alumina [10,27] and react with adsorbed pollutants on the catalytic surface. TBA inhibits hydroxyl radicals in the solution, hence fewer hydroxyl radicals may be available to adsorb on catalyst surface. The phosphate effect also supports this hypothesis. The more the adsorption of phosphates, the fewer surface reactions of adsorbed radicals with pollutants will take place as phosphates are hydroxyl radical scavengers.

The lack of catalytic activity at pH 13.0 may possibly be due to the adsorption of hydroxide ions that restrict the adsorption of pollutants on the surface. Additionally, reactions inside the solution are faster at this pH.

4.5. The reuse performance experiments

The long-term performance of the ozonation of ibuprofen on alumina has been investigated in tap and deionised water. The results presented in Fig. 10 show that the catalytic activity of alumina does not change even after > 300 min ozonation time in

deionised water. However, in the case of tap water the catalytic activity was significantly affected. This may be due to the naturally present constituents in tap water that may adsorb on the surface of alumina and poison it. Thus the results further support our hypothesis that surface reactions are vital in ozonation of pollutants in the presence of alumina. It is important to mention here that the reuse efficiency of Al₂O₃/O₃ decreased significantly in drinking water as compared with its efficiency in deionised water. However, when the reuse performance experiments were compared with ozonation alone at the same conditions (Fig. 1), the ibuprofen % removal was still found to be high, even after 300 min in natural water. For example, the % removal of ibuprofen was 52% in 360 min (Fig. 10) and in the case of ozonation alone it was only 39.5% (Fig. 1).

The SEM micrographs of fresh and used alumina in the reuse performance experiments (tap water) are presented in Fig. 11.

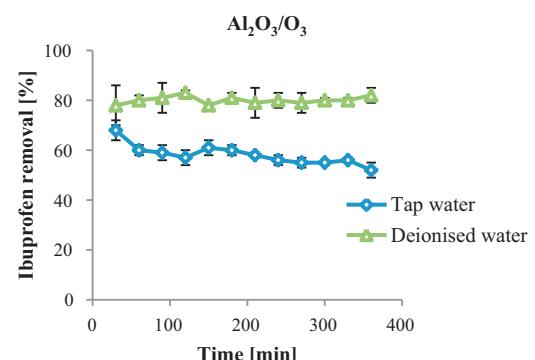


Fig. 10. Reuse performance experiments for removal of ibuprofen by Al₂O₃/O₃ ($C_{0(\text{ibu})} = 15 \text{ mg/L}$; $T = 20^\circ\text{C}$; $O_3 = 0.5 \text{ mg/min}$; pH = 7.2; catalyst = 5.0 g; $V = 490 \text{ mL}$).

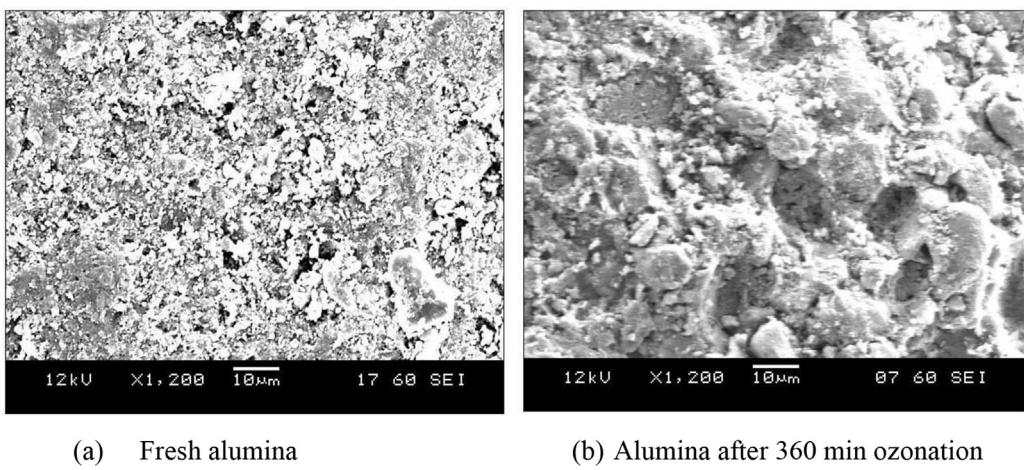


Fig. 11. SEM of alumina before and after its application in the removal of ibuprofen in tap water by $\text{Al}_2\text{O}_3/\text{O}_3$ ($C_{\text{O}_3(\text{ibu})} = 15 \text{ mg/L}$; $T = 20^\circ\text{C}$; $\text{O}_3 = 0.5 \text{ mg/min}$; $\text{pH} = 7.2$; catalyst = 5.0 g; $V = 490 \text{ mL}$).

The figure clearly indicates that catalytic ozonation on alumina in drinking water significantly affects the topography of alumina's surface. Based on the previous reports [2] it is hypothesised that this may be due to the presence of inorganic ions and organic matter adsorbed on the surface of water. The above results further support our hypothesis that surface reactions are important in the case of catalytic ozonation on alumina.

5. Conclusions

This study concludes that alumina catalyses the degradation of pollutants via radical mechanism and surface reactions play an important role in the removal of pollutants. The following are the main conclusions.

1. Alumina's activity depends on its ability to adsorb pollutants which is directly related to the hydrophilic nature of pollutants.
2. Catalytic ozonation on alumina proceeds via a hydroxyl radical mechanism with pollutants.
3. TBA, phosphates and humic acid were found to influence catalytic activity of alumina.
4. Surface reactions are important for the effective removal of pollutants on alumina.

Acknowledgments

The financial support from the University of Engineering and Technology Lahore (Pakistan) and the University of Huddersfield (United Kingdom) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.10.010>.

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